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1 Introduction

Various kinds of alloy steel powders for use in high strength sintered products have been developed to reduce the size and weight of automobile parts, which are the main application of Fe-based sintered steels[1]. To strengthen the sintered steel for as-sintered use, relatively large amounts of a noble alloying element such as Ni have been used[2]. Another recent development for strengthening is a technique of rapid cooling after sintering[3]. This process, however, has not yet gained wide acceptance, since it requires a new sintering furnace with a rapid cooling system.

The present authors have investigated production method to attain high strength sintered steels without adding a large amount of alloying element at a cooling rate of 5–30°C/min in a conventional sintering furnace. It is important, in strengthening sintered steels without heat-treatment, to adjust microstructures by optimizing alloying compositions for the cooling rate in a sintering furnace, since microstructures cannot be adjusted by rolling. The compressibility of steel powders is also important to enhance the sintered density, which is directly related with sintered properties, and to prolong the life of powder compaction dies since the lower applied pressure is need to obtain the compact with the same density.

The new alloying compositions of Cr-alloyed steel powder have been investigated on the basis of KIP 4100 V (1Cr-0.3Mo-0.7Mn) steel powder[4,5] which is Ni-free and has shown good wear resistance in automobile sintered and case-hardened parts. The effects of Cr, Mn and Mo contents on the compressibility of the powder and the strength of the sintered compacts have also been investigated, as has the strengthening of the sintered compacts by adding V, which is used as a precipitation hardening element in non-tempered steel[6] and rail steel[7].

There are two alloying methods for steel powders, i.e., prealloying and partially alloying. Prealloying provides better homogeneity of the microstructure of the sintered compacts and partially alloying provides better compressibility of the powder. Vacuum annealing which is an original process of ours[8] has been conducted to lower C, O and N contents and obtain high compressibility of the prealloyed steel powders in this investigation.

As a result of these investigations, KIP 103 V (prealloyed 1Cr-0.3Mo-0.3V) has been developed to obtain high compressibility and high strength of sintered compacts without heat-treatment after sintering[9,10].

This paper describes the effect of alloying elements (Cr, Mn, Mo and V) on the compressibility of Cr alloyed steel powders and the effect of alloying elements (Mn, Mo and V) on the relationship between cooling rate after sintering and strength for the sintered compacts.

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Table 1 Chemical compositions of powders used

(mass%)

	Cr	Mn	Mo	V	Ni	Cu
0.5Cr	0.50	0.05	0.01	—	—	—
1Cr	1.09	0.02	0.01	—	—	—
2Cr	2.05	0.04	0.01	—	—	—
3Cr	3.18	0.05	0.01	—	—	—
1Cr-0.3Mo-0.7Mn	0.93	0.64	0.32	—	—	—
1Cr-0.3Mo-0.3V	1.07	0.01	0.32	0.29	—	—
1Cr-0.25Mo	0.99	0.02	0.24	—	—	—
1Cr-0.3Mo	0.97	0.08	0.35	—	—	—
1Cr-0.4Mo	0.98	0.02	0.40	—	—	—
4Ni-1.5Cu-0.5Mo*	—	—	0.50	—	4.2	1.5

*Partially-alloyed

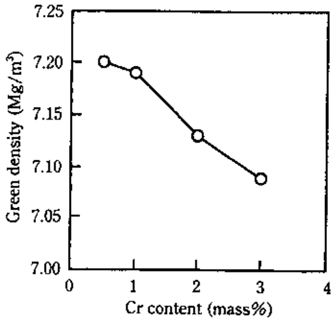

Fig. 1 Effect of Cr content on compressibility of Cr alloyed steel powder

2 Experiments

2.1 Effects of Alloying Elements on the Compressibility of Cr Alloyed Steel Powders

An experiment was performed using the water atomized and vacuum annealed Cr alloyed steel powders. **Tabel 1** shows the chemical compositions of the powders used. The powders were mixed with 1 mass% zinc stearate as a lubricant and compacted at 490, 588 and 686 MPa into cylindrical shape of 11.3 mm in diameter and 10 mm in height. The density of the green compacts was measured.

2.2 Effects of Alloying Elements on the Strength of Cr Alloyed Sintered Steels

The 1 mass% Cr alloyed steel powders were mixed with 0.9 mass% graphite and 4Ni-1.5Cu-0.5Mo steel powder was mixed with 0.6 mass% graphite, as these are the compositions that provide the highest strength after sintering, respectively. The mixed powders were compacted to a green density of 7.0 Mg/m^3 with die lubrication and sintered at 1 150°C for 60 min in an atmosphere of N_2, then cooled at rates of 1 to 50°C/min. The cooling rates are average values in the temperature range between 700 and 400°C, in which the transformation temperature, Ar_3 exists. The sintered compacts were machined into round bar-shaped test pieces of 5 mm in diameter and 15 mm in parallel portion length. The room temperature tensile test was carried out at a rate of 5 mm/min.

The 1Cr-0.3Mo-0.3V, 1Cr-0.3Mo and 1Cr-0.3Mo-0.7Mn steel powders were mixed with 0.9 mass% graphite and 1 mass% zinc stearate as a lubricant and compacted at 686 MPa. They were sintered at 1 150°C for 60 min in an atmosphere of 90 vol% N_2 and 10 vol% H_2 and cooled at a rate of about 20°C/min. The sintered compacts were machined into unnotched round bar-shaped test pieces of 8 mm in diameter and 15.4 mm in parallel portion length for the Ono-type rotating bending fatigue test. The endurance limit was defined as the million-cycle fatigue strength. The wear resistance of the sintered compacts was measured at a velocity of 4.21 m/s and a load of 124 N by the Ohgoshi-method.

The microstructure of the sintered compacts was observed with an optical microscope after etching their cross-section in 3% nital. The spacing of the pearlite lamellar in the sintered compacts was measured by SEM imaging with an acceleration voltage of 15 kV after etching the polished surface of their cross-section in picral. Five cut lines were drawn in each of ten areas (fields of view), and the spacing was calculated by Eq. (1)[11]:

$$\lambda = m/2 \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots (1)$$

where λ: average lamellar spacing, m: average interecept length on cut lines which cross pearlite lamellar

The inclusions produced in the sintered compacts were quantified by the Br_2-methanol method and determined by X-ray analysis of the extracted residue. The fractured surface after tensile test was observed with SEM with an acceleration voltage of 15 kV and the inclusion in the bottom of the fractured surface was analyzed by EDX.

3 Results

3.1 Effects of Alloying Elements on the Compressibility of Cr Alloyed Steel Powders

The effects of Cr content on the compressibility of Cr alloyed steel powders is shown in **Fig. 1**. Cr content was fixed to 1 mass%, since the green density declined remarkably when Cr content exceeded 1 mass%. The effects of Mn and V contents on the compressibility of Cr alloyed steel powders are shown in **Fig. 2**. The green density increased by an amount of more than 0.1 Mg/m^3 with a decrease in Mn content from 0.7 mass% to 0.08 mass%, but decreased as much as 0.04 Mg/m^3 with the addition of 0.3 mass% V content. The reduction of compressibility by the increase in Cr, Mn and V content was caused by solid solution hardening. Mo had no effect on the compressibility of the powder in a range between 0.25 and 0.4 mass%.

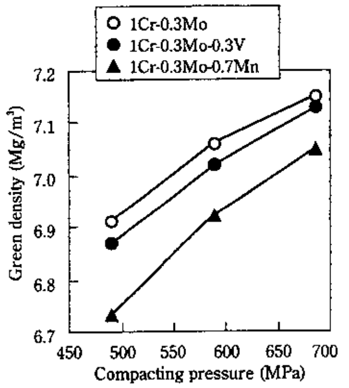

Fig. 2 Effect of Mn and V contents on compressibility of Cr alloyed steel powder

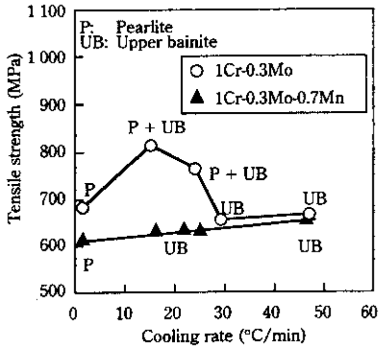

Fig. 3 Effect of Mn on the relationship between cooling rate and tensile strength of Cr-Mo sintered steels

3.2 Effects of Alloying Elements on the Strength of Cr Alloyed Sintered Compacts

The relationship between the cooling rate and tensile strength of the 1Cr-0.3Mo-0.7Mn and 1Cr-0.3Mo sintered steels is shown in **Fig. 3**. The microstructure observed with an optical microscope is noted within the figure. The tensile strength of the 1Cr-0.3Mo-0.7Mn sintered steel increased slightly as the cooling rate increased. On the other hand, the maximum strength of 1Cr-0.3Mo sintered steel was obtained when the cooling rate was 15°C/min, and was 200 MPa higher than that of 1Cr-0.3Mo-0.7Mn sintered steel. The strength of the 1Cr-0.3Mo sintered steel declined when the cooling rate was higher than 15°C/min and there were no differences between the strengths of both sintered steels at a cooling rate higher than 30°C/min. The microstructure of the 1Cr-0.3Mo sintered steel was a fine pearlite, a coarse upper bainite or a combination of these structures, as shown in **Photo 1**. The pearlite lamellar spacing narrowed and the fraction of coarse upper bainite increased as the cooling rate increased.

The relationship between cooling rate and tensile strength of the Cr-Mo sintered steels, which has various

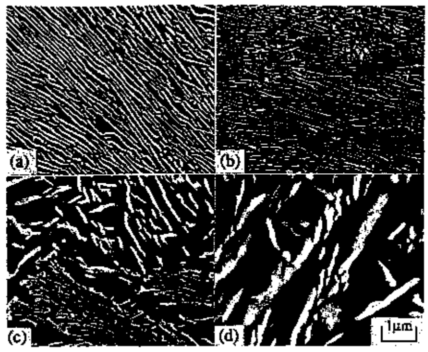

Photo 1 Microstructures of 1Cr-0.3Mo sintered steel at cooling rates of (a) 1°C/min, (b) 15°C/min, (c) 24°C/min, and (d) 47°C/min

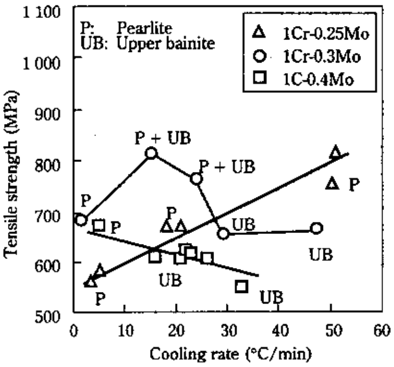

Fig. 4 Effect of Mo on the relationship between cooling rate and tensile strength of Cr-Mo sintered steels

Mo contents and no Mn, is shown in **Fig. 4**. The microstructure observed with an optical microscope is noted within the figure. The 1Cr-0.25Mo sintered steel had a fine pearlite structure in the cooling rates of 1–50°C/min and the strength of the sintered steel increased with the cooling rate. On the other hand, the strength of the 1Cr-0.4Mo sintered steel decreased slightly as the cooling rate increased owing to the formation of coarse upper bainite at a cooling rate of higher than 17°C/min.

The relationship between cooling rate and tensile strength for 1Cr-0.3Mo-0.3V, 1Cr-0.3Mo and 4Ni-1.5Cu-0.5Mo sintered steels is shown in **Fig. 5**. The tensile strength of 1Cr-0.3Mo-0.3V sintered steel increased as the cooling rate increased, reaching 1 000 MPa with a fine pearlite at 33°C/min. Compared with the 1Cr-0.3Mo sintered steel, the tensile strength of the 1Cr-0.3Mo-0.3V sintered steel was higher at a cooling rate of 1–30°C/min and the range of cooling rate for obtaining strength higher than 800 MPa was wider. The strength of 1Cr-0.3Mo-0.3V sintered steel was higher than that of 4Ni-1.5Cu-0.5Mo sintered steel in the cooling rate range

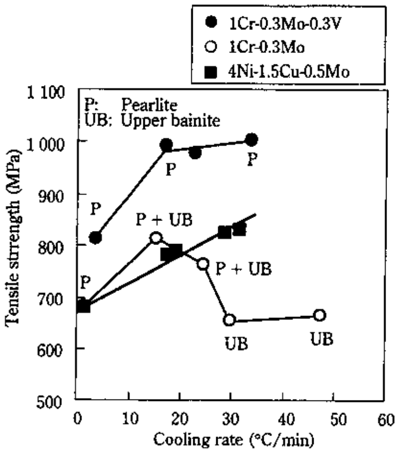

Fig. 5 Relationship between cooling rate and tensile strength of Cr-Mo and 4Ni-1.5Cu-0.5Mo sintered steels

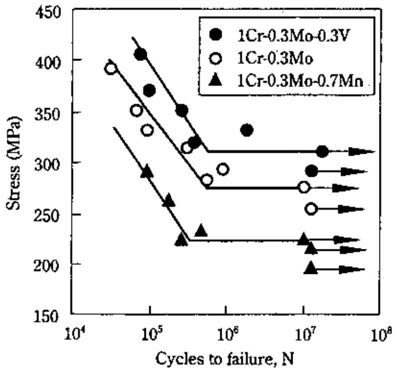

Fig. 6 Rotating bending fatigue strength of Cr-Mo sintered steels

of 1–30°C/min.

Accordingly, it is obvious that 1Cr-0.3Mo-0.3V steel powder has high compressibility and provides high strength for sintered compacts without heat-treatment after sintering.

3.3 Fatigue Properties and Wear Resistance of 1Cr-0.3Mo-0.3V Sintered Steel

The rotating bending fatigue strength of the Cr-Mo sintered steels is shown in **Fig. 6**. The fatigue limit of the 1Cr-0.3Mo-0.3V sintered steel which was greater than 310 MPa was higher than that of the 1Cr-0.3Mo and 1Cr-0.3Mo-0.7Mn.

The relationship between wear volume and wear distance for the Cr-Mo sintered steels is shown in **Fig. 7**. The 1Cr-0.3Mo-0.3V sintered steel shows lower wear than volume the 1Cr-0.3Mo and 1Cr-0.3Mo-0.7Mn sintered steel. Therefore the 1Cr-0.3Mo-0.3V sintered steel has good wear resistance.

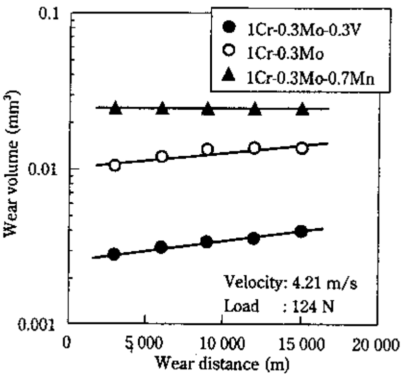

Fig. 7 Relationship between wear volume and wear distance for Cr-Mo sintered steels by the Ohgoshi wear test

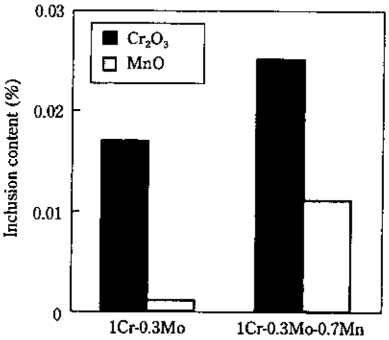

Fig. 8 Inclusion content analysis by Br_2-methanol method of Cr-Mo sintered steels

4 Discussion

Figures 3–5 indicate that the tensile strenght of the sintered steels increased because of the reduction of Mn content, optimization of Mo content and the addition of V. The mechanism responsible for these improvements will be discussed in the following.

Mn has a strong affinity to oxygen and a high hardenability. This suggests that the strength is improved because Mn oxides are reduced and microstructure is changed by the reduction of Mn.

The relationship between inclusion content and Mn content of the Cr-Mo sintered steels is shown in **Fig. 8**. The inclusion content apparently decreased as Mn content decreased. SEM micrographs of fractured surfaces of 1Cr-0.3Mo and 1Cr-0.3Mo-0.7Mn sintered steel are shown in **Photo 2**. There are no inclusions in the 1Cr-0.3Mo sintered steel. However, there are many inclusions in the bottom of fractured surface of the 1Cr-0.3Mo-0.7Mn sintered steel. These inclusions were determined to be $MnO \cdot Cr_2O_3$ spinel oxide by EDX and X-ray analysis of the residue extracted by the Br_2-methanol method[5]. The reduction of this oxides caused the improvement in strength.

The fraction of upper bainite structure increased and

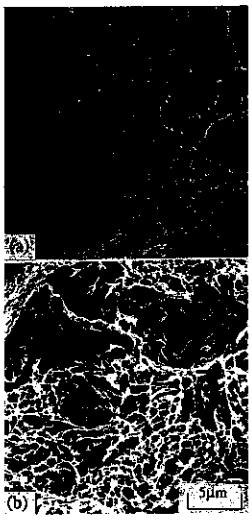

Photo 2 SEM micrographs of fractured surfaces of Cr-Mo alloyed sintered steels; (a) 1Cr-0.3Mo, (b) 1Cr-0.3Mo-0.7Mn

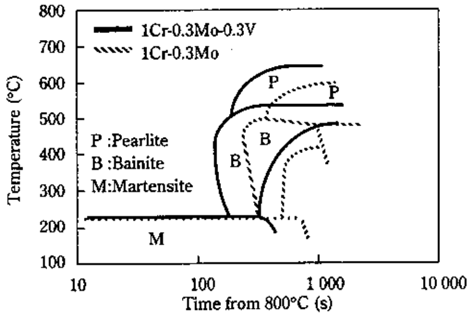

Fig. 9 CCT diagrams of Cr-Mo sintered steels

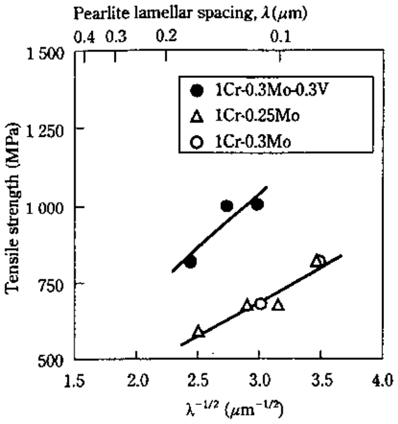

Fig. 10 Relationship between pearlite lamellar spacing and tensile strength of Cr-Mo sintered steels

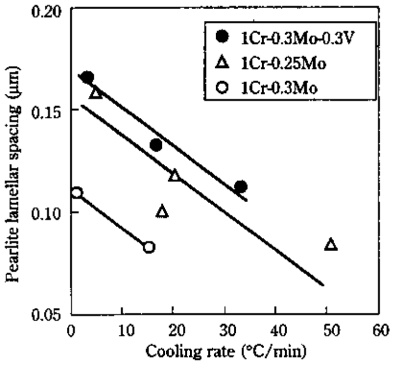

Fig. 11 Relationship between cooling rate and pearlite lamellar spacing of Cr-Mo sintered steels

the tensile strength decreased when the sintered steel contained either Mn or 0.3–0.4 mass% Mo at the cooling rate of higher than 15°C/min. This was likely because the strength of the coarse upper bainite was lower than that of the fine pearlite, as was also mentioned in an investigation of hyper-eutectoid steel wire[12].

The addition of V to the 1Cr-0.3Mo steel enhanced the tensile strength and gave a wider cooling rate range, where more than 800 MPa of tensile strength was obtained, much higher than that of the 1Cr-0.3Mo steel. The mechanism responsible for these improvements will be discussed in the following.

The CCT diagrams of the 1Cr-0.3Mo-0.3V and 1Cr-0.3Mo sintered steels are shown in **Fig. 9**. The addition of V lowered hardenability as discussed previously in connection with high carbon Cr steels[13] and extended the range for pearlite structure, which gave higher tensile strength than the coarse upper bainite structure. Consequently, the additon of V also extended the range of cooling rate after sintering so that high strength could be obtained.

It has been known that the inverse square of the pearlite lamellar spacing in pearlitic steel has a linear relation with tensile strength[14]. This relationship is shown in **Fig. 10** for the Cr-Mo sintered steels in the range of cooling rate for obtaining pearlitic structure. The tensile strength linearly increased as the lamellar spacing decreased for the 1Cr-0.25Mo and 1Cr-0.3Mo sintered steels without V. The 1Cr-0.3Mo-0.3V sintered steel had a similar linear relation. But, its tensile strength was higher than that of the V-free sintered steel at the same lamellar spacing. The relationship between cooling rate and pearlite lamellar spacing of Cr-Mo sintered steels is shown in **Fig. 11**. The pearlite lamellar spacing decreased as the cooling rate increased for all the sintered steels tested. At the same cooling rate, however, the lamellar spacing narrowed as the Mo content increased and widened with the addition of V. Thus it is obvious that the increase in tensile strength obtained by adding V can not be explained by the narrowing lamellar spacing.

The precipitation of V was studied in an extractive replica of the 1Cr-0.3Mo-0.3V sintered steel, because

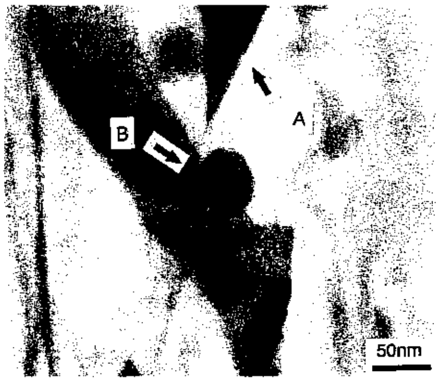

Photo 3 TEM micrograph of extractive replica of 1Cr-0.3Mo-0.3V sintered steel at a cooling rate of 24°C/min

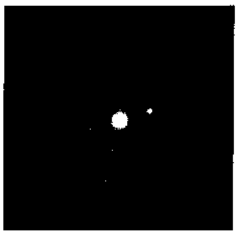

Photo 4 Electron diffraction pattern of the precipitate (B) in Photo 3

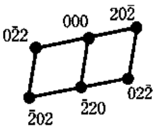

Fig. 12 Key diagram for Photo 3

the investigation of non-tempered steel[6] and rail steel[7] has indicated that the increase in tensile strength by adding V is attributed to the precipitation of V. In **Photo 3**, cementite (A) and fine precipitates (B) can be observed. The fine precipitates (B) are identified as vanadium nitrides by their electron diffraction pattern, as shown in **Photo 4** and **Fig. 12**. The precipitates in the sintered steel seem to be vanadium carbonitrides, because nitrogen atoms in nitrides with a face-centered cubic structure can be substituted easily by carbon atoms, and V precipitates often take the form of V (C, N) in steel[15]. Thus, we concluded that the increase in strength was caused by the precipitation of fine vanadium carbonitrides.

5 Conclusions

The new KIP 103 V (prealloyed 1Cr-0.3Mo-0.3V) steel powder has been developed to provide high powder compressibility and high strength of sintered compacts without heat-treatment after sintering. The main results obtained are summarized as follows:

(1) The compressibility of the Cr alloyed steel powder declined because of solid solution hardening when Cr content exceeded 1 mass%.

(2) When Mn content decreased 0.08 mass% from 0.7 mass% in the Cr alloyed steel powder, the compressibility of the steel powder improved because of the reduction of solid solution hardening, and the strength of the sintered steel increased because of the reduction of oxides and the restrained production of coarse upper bainite.

(3) When V content was 0.3 mass% in the Cr alloyed steel powder, the compressibility of the steel powder declined slightly because of solid solution hardening and the strength of the sintered steel increased because of the precipitation of vanadium carbonitrides.

(4) The 1Cr-0.3Mo-0.3V sintered steel extended the range for pearlite structure within which high strength, high tensile strength (1 000 MPa), high rotating bending fatigue limit (310 MPa) and good wear resistance could be obtained.

(5) The high strength of 1Cr-0.3Mo-0.3V sintered steel was attributed to a narrow pearlite lamellar spacing, a decrease in Mn oxide and precipitation hardening by vanadium carbonitrides.

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